

REPORT DOCUMENTATION PAGE

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14. ABSTRACT

15. SUBJECT TERMS

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MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO)

19 Apr 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2001-096**
Shawn H. Phillips; Timothy S. Haddad; Rusty L. Blanski, "New Multi-Functional Materials Using Versatile Hybrid (Inorganic/Organic) POSS Nanotechnology"

International Symposium – SAMPE
(Long Beach, CA, 08 May 2001) (Deadline: 08 May 01)

(Statement A)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.

Comments: _____

Signature _____ Date _____

2. This request has been reviewed by the Public Affairs Office for: a.) appropriateness for public release and/or b) possible higher headquarters review.

Comments: _____

Signature _____ Date _____

3. This request has been reviewed by the STINFO for: a.) changes if approved as amended, b) appropriateness of references, if applicable; and c.) format and completion of meeting clearance form if required

Comments: _____

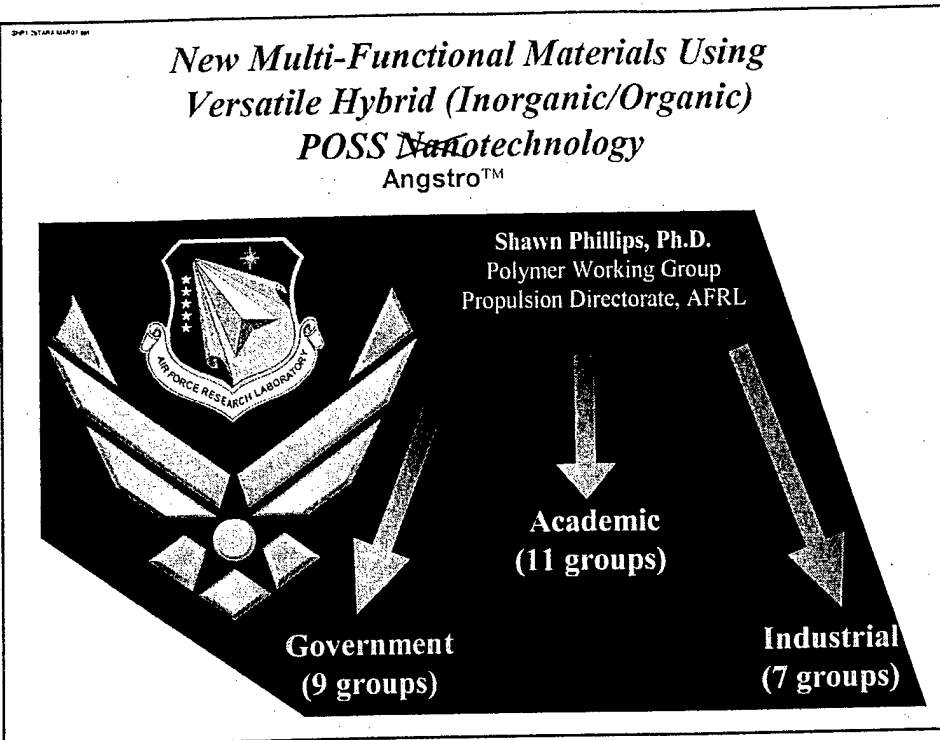
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4. This request has been reviewed by PR for: a.) technical accuracy, b.) appropriateness for audience, c.) appropriateness of distribution statement, d.) technical sensitivity and economic sensitivity, e.) military/national critical technology, and f.) data rights and patentability

Comments: _____

APPROVED/APPROVED AS AMENDED/DISAPPROVED

PHILIP A. KESSEL Date
Technical Advisor
Space and Missile Propulsion Division



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Acknowledgements

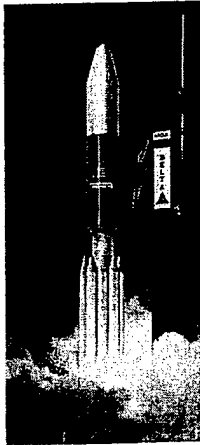
<u>Polymer Working Group</u>	<u>External</u>
Dr. Tim Haddad*	Prof. Frank Feher - UCI
Dr. Rusty Blanski*	Prof. Andre Lee* - MSU
Dr. Brent Viers*	Dr. Joe Lichtenhan - HP
Capt Rene Gonzalez*	Dr. Joe Schwab - HP
Brian Moore*	Prof. Pat Mather - UConn
Capt Steve Svejda, Ph.D.	Dr. Jeff Gilman* - NIST
Justin Leland	Prof. Ben Hsiao - SUNY SB
Pat Ruth	Prof. Bryan Coughlin* - UMass
New Post-Doc: Polymer Synthesis	Prof. Gar Hoflund - UF
	Dr. Barry Farmer - AFRL/MLBP
<u>Edwards</u>	Dr. Rich Vaia* - AFRL/MLBP
Dr. Kevin Chaffee	Dr. Seng Tan - WMR
Mr. Paul Jones	Prof. Mark Gordon* - Iowa St. U
Mr. Hieu Nguyen	Dr. Howard Katzman - Aerospace
	Mr. Don Geidt/Mike Blair - CSD/Thiokol

Funding: AFOSR (Dr. Charles Lee), AFRL, Hybrid Plastics

Basic R&D Applications R&D

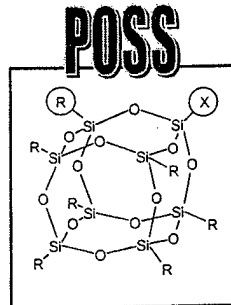
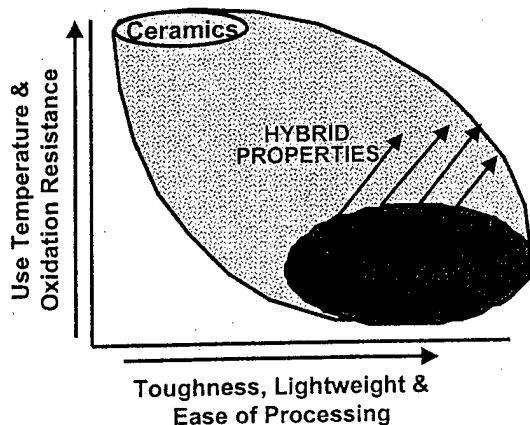
"Hot" Topics in Propulsion/Air Force Materials

POSS Nanostructured Polymers



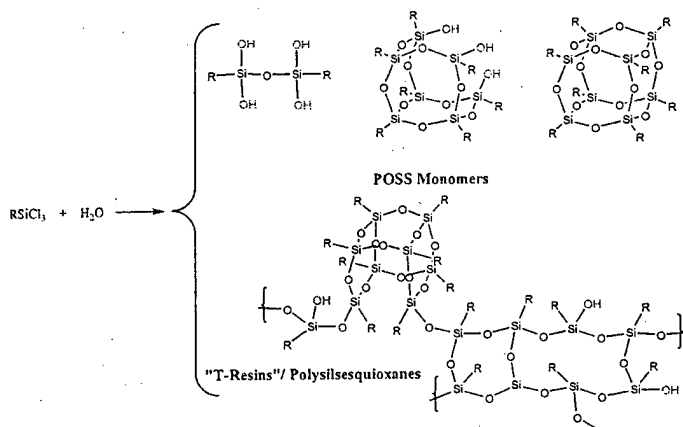
- High Temperature Insulation for Solid Rocket Motors
- Capacitors
- High Temperature/Lightweight Jet Canopies
- Space-survivable Materials and Coatings
- Low/High Temp. Hybrid Lubricants
- Plastic Tubing and Ducting for Liquid Rocket Engines
- High Temperature/High Translation Strength Composites
- Improved Radome Materials

Multiple Applications/ Multi-Function



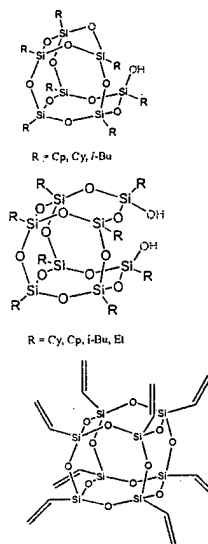
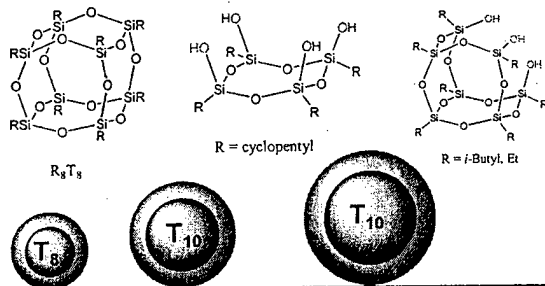
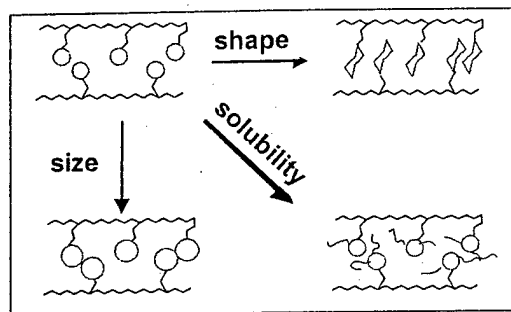
- Improve High Performance Polymers
- Transform Commodity Polymers into High performance Polymers
- Develop Multi-Functional Materials

POSS Feedstocks



- R = Cyclohexyl, t = 3-36 (48 months)
- R = Cyclopentyl, t = 11 days!
- No other incompletely condensed silsesquioxanes

Existing POSS-Polymers: Structure/Property Relationships



Property Enhancements via POSS

Observed in POSS-Copolymers and Blends

increased T_g

increased T_{dec}

enhanced blend
miscibility

reduced
flammability

extended
temperature range

oxidation
resistance

reduced
heat evolution

increased
oxygen permeability

altered
mechanicals

lower density

lower thermal
conductivity

reduced
viscosity

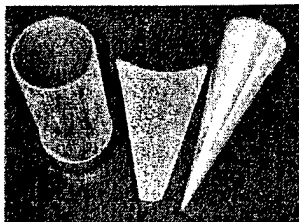
disposal
as silica

thermoplastic
or curable

Bear
competitors'
patents!

6.2 (IHPRPT): Solid Rocket Motor Insulation

Case Insulation



POSS-Insulation Sample

**Goal: 50% Lower Erosion of Insulation (44 % weight reduction,
7.4% booster payload increase) – Phase III IHPRPT**

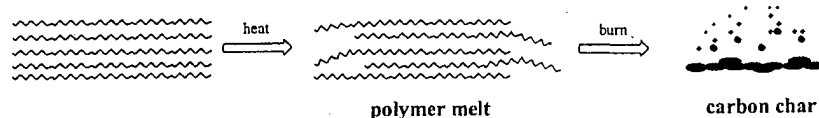
Objective: Development of Ceramic Forming Polymer

POSS-Polymer Insulation - Advantages:

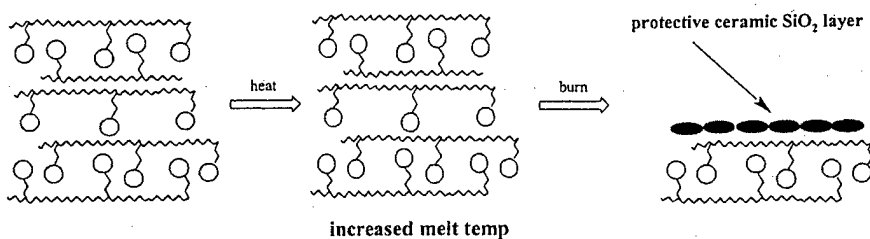
- High loadings of POSS can be incorporated without embrittlement
- Si to O ratio is 1:1.5, proven to oxidize up to 1:2 (SiO_2)
- Tailorability of POSS monomers improve physical/mechanical properties
- Capabilities for Large and Small scale testing (Hybrid Plastics)

POSS for Flame Retardant Materials

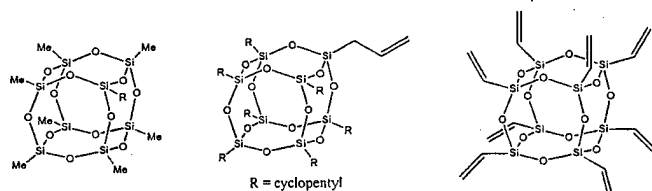
Traditional Polymer



POSS Polymer



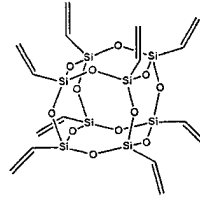
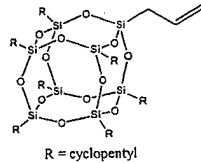
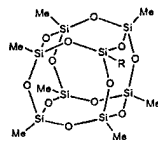
Comparisons of POSS in EPDM



At 25 wt% loadings relative to a proprietary base-line material

Hardness:	12%↑	no change	no change
Tensile:	17%↓	17%↓	---
Elongation:	no change	no change	no change
Viscosity:	42%↓	39%↓	36%↓
Density:	9%↑	3% ↓	3% ↓

Comparisons of POSS in EPDM



At 50 wt% loadings relative to a proprietary base-line material

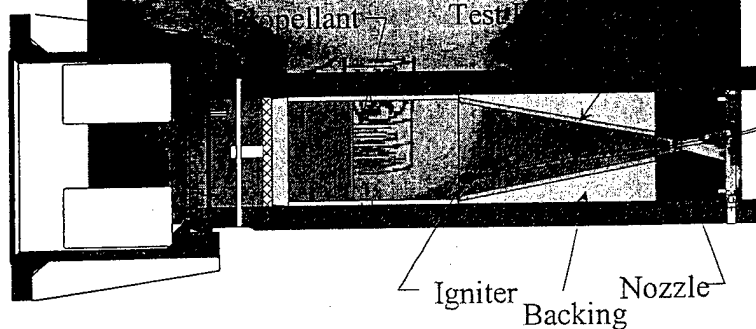
Hardness:	15%↑	no change	17%↑
Tensile:	5%↓	27%↓	1%↓
Elongation:	no change	no change	no change
Viscosity:	35%↓	21%↓	36%↓
Density:	15%↑	3% ↓	12%↑

In-House SRM Insulation Testing

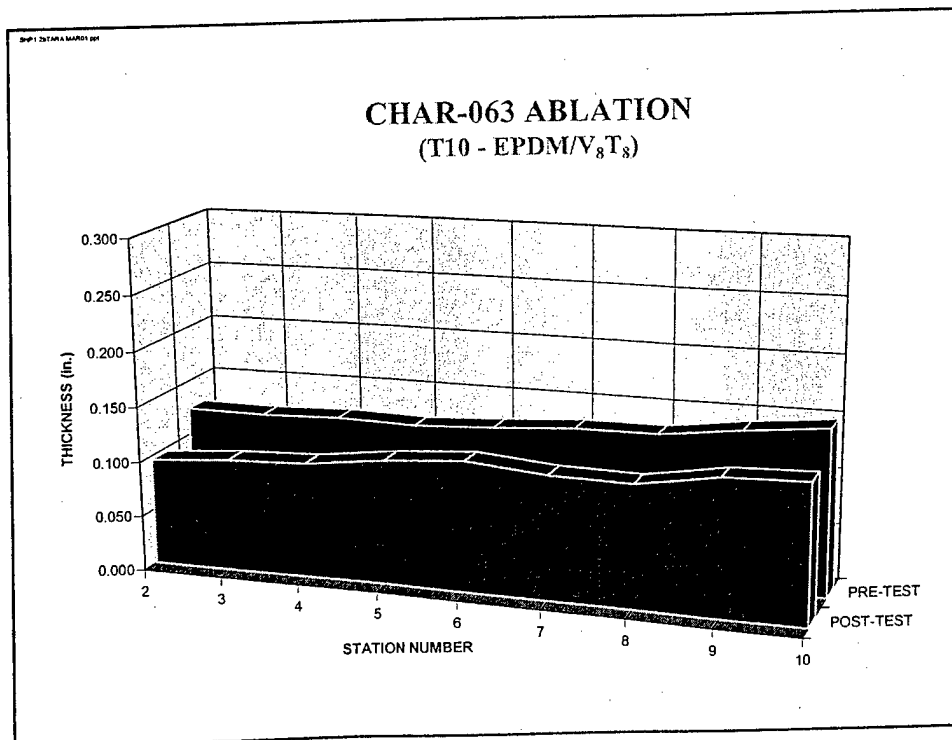
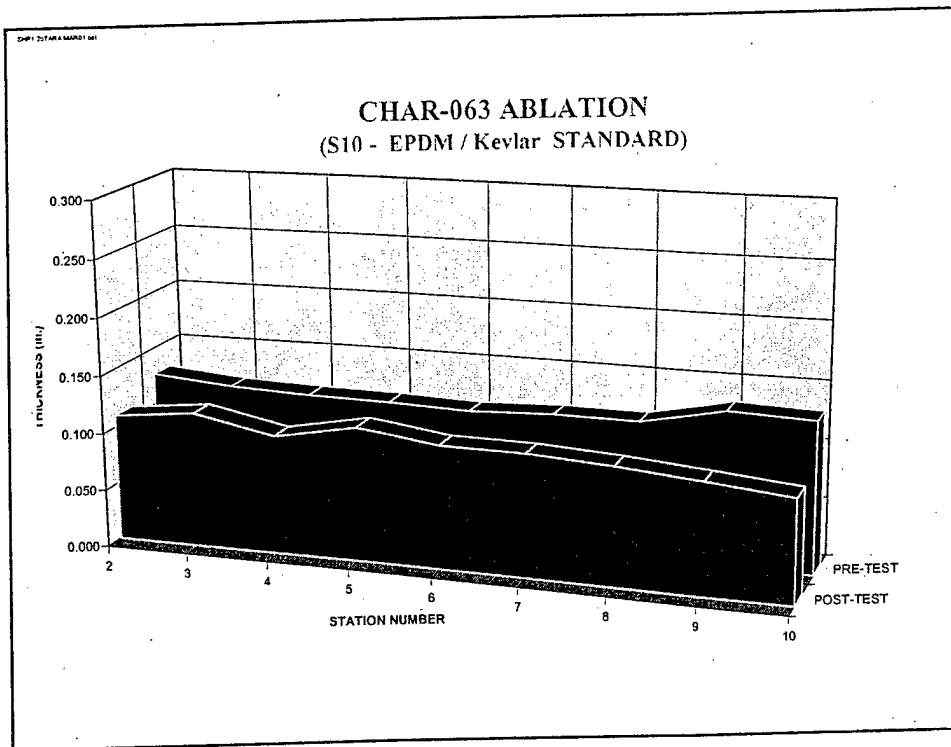
Objective: Low Cost/Low Volume Materials Screening for SRM Insulation

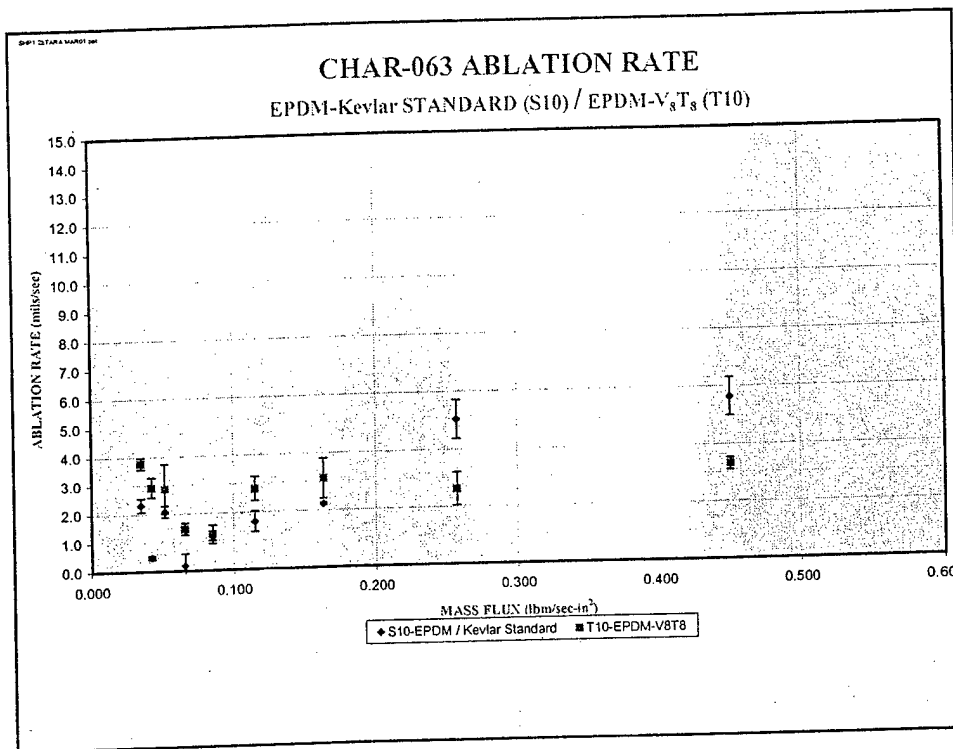
Capabilities

- Edward (Pi-K Motor): volume reduction (5 kg to 15 g)
- Total Cost: synthesis, part fabrication, analysis
- Rapid turn: 6 samples per day



Firing
Video
Clip





Solid Rocket Motors/Insulation

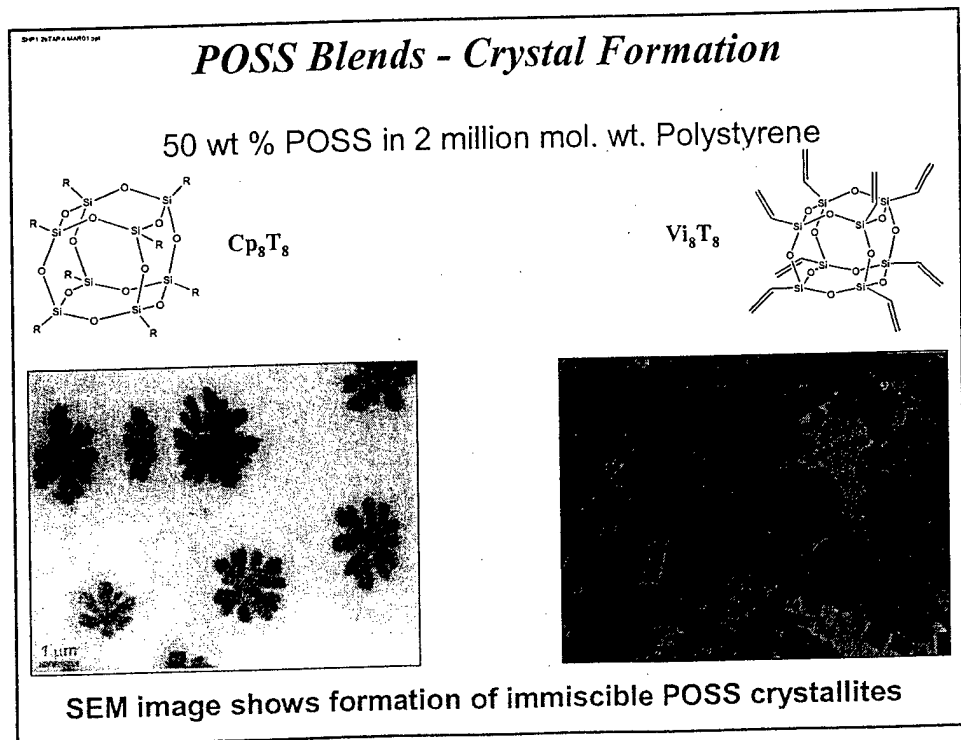
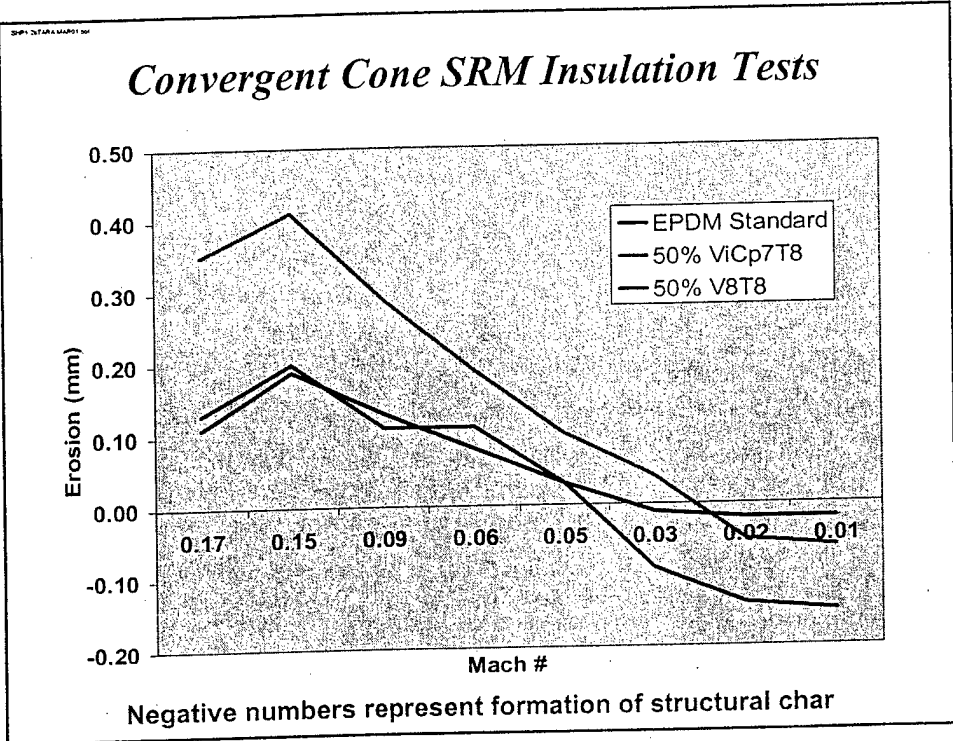
A
B
C

A) Insulation containing POSS monomers

B) Convergent Cone

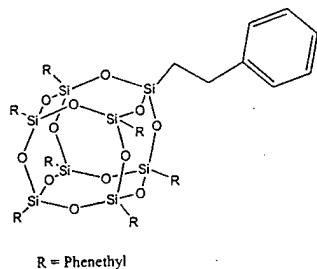
C) Convergent Cone + Insulation

R = cyclopentyl



POSS Blends - Miscibility

50 wt % Phenethyl₈T₈ in 2 million mol. wt. Polystyrene



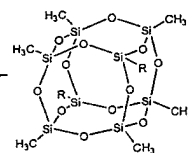
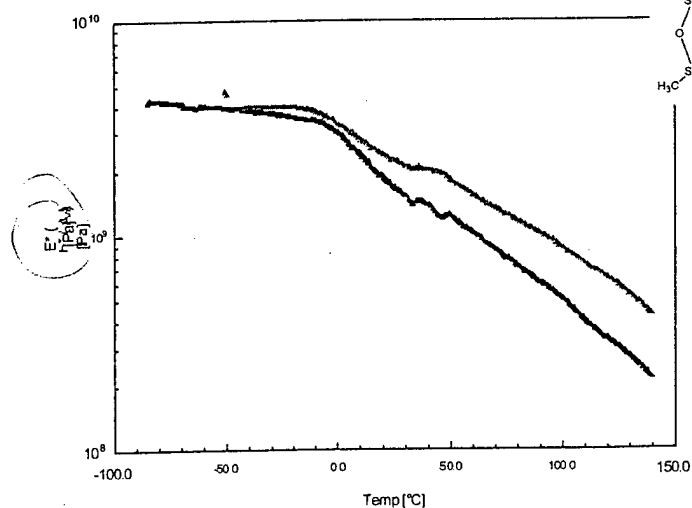
- Catalytic hydrogenation of Styryl₈T₈
- Demonstrated Complete Miscibility!!
- No POSS crystallites by SEM or X-ray!!



Scale-up, incorporation and testing polymer systems

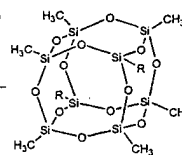
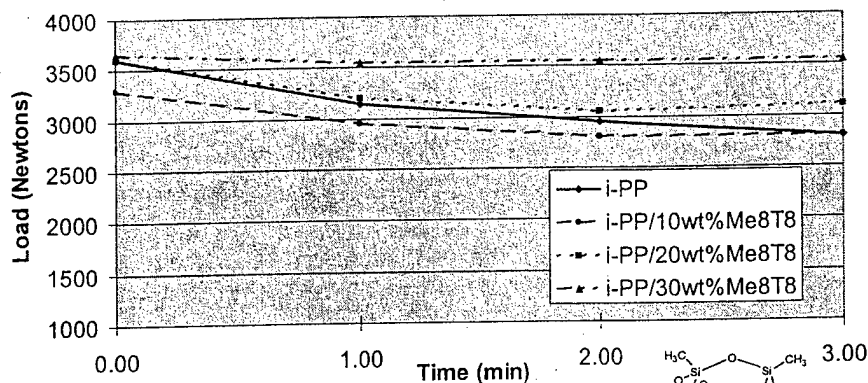
i-PP/Me₈T₈ Processing Studies

Neat Polypropylene and Blended with POSS nano-fillers



i-PP/Me₈T₈ Processing Studies

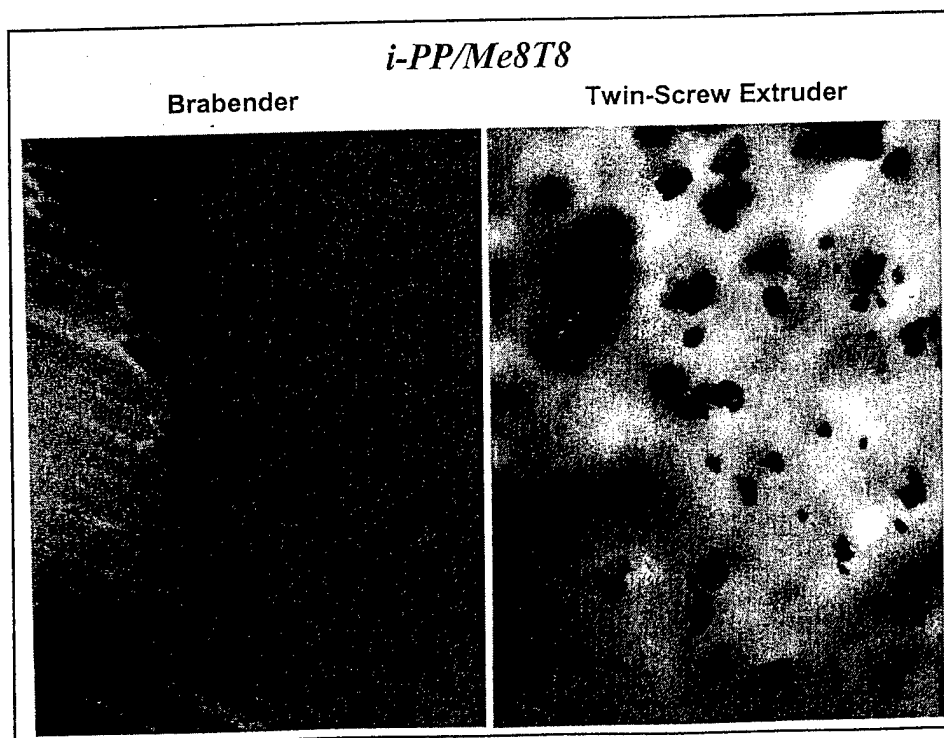
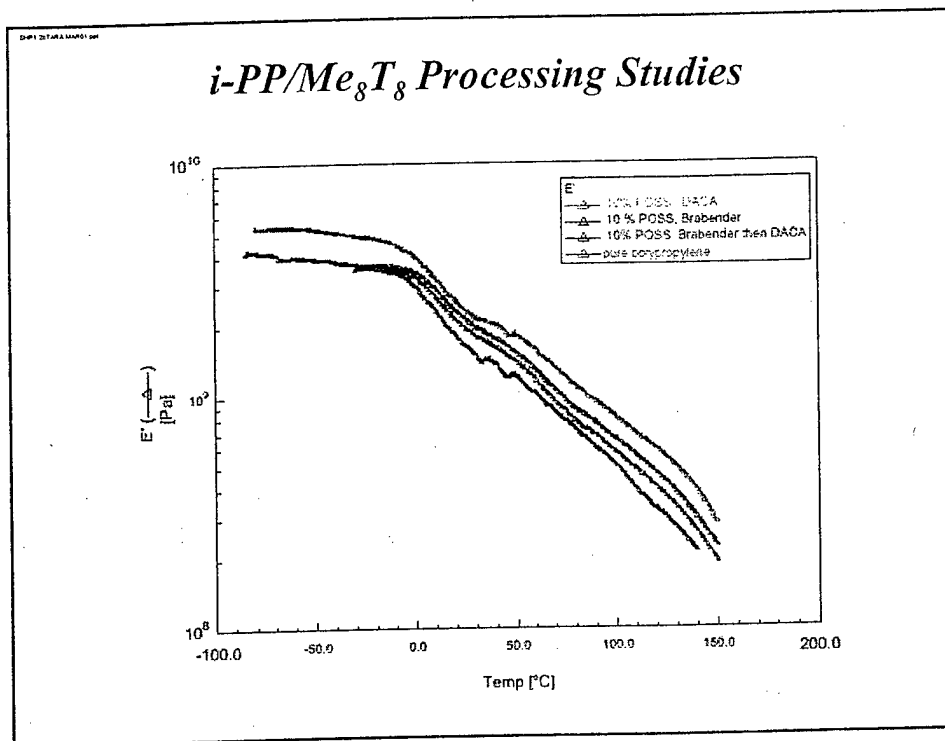
iso-Polypropylene w/ Me8T8



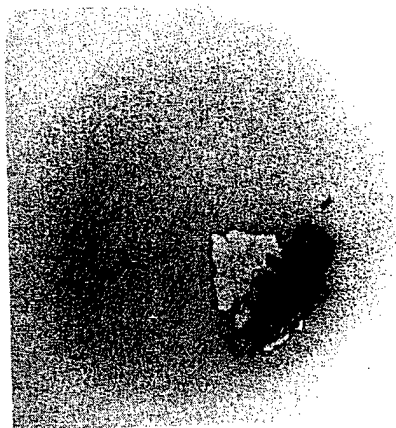
Prof. Andre Lee - Michigan State University

	Dow data	Neat <i>i</i> -PP (processed)	<i>i</i> -PP blended 2 wt% Methyl ₈ T ₈	<i>i</i> -PP blended 5 wt% Methyl ₈ T ₈	<i>i</i> -PP blended 10 wt% Methyl ₈ T ₈
Tensile Strength @ Yield; ASTM D638	5000 psi (34.5 MPa)	4800 psi (33.0 MPa)	5000 psi (34.5 MPa)	5100 psi (35.1 MPa)	5200 psi (35.8 MPa)
Flexural Modulus (0.05 in/min, 1% secant); ASTM D790A	240,000 psi (1.655 GPa)	235,000 psi (1.620 GPa)	251,000 psi (1.730 GPa)	255,000 psi (1.757 GPa)	262,000 psi (1.80 GPa)
HDT @ 66 psi, as injected; ASTM D648	210 °F (99 °C)	210 °F (99 °C)	221 °F (105 °C)	239 °F (115 °C)	255 °F (124 °C)
Impact Izod @25C ASTM D256A	0.5 ft-lb/in	0.55 ft-lb/in	0.55 ft-lb/in	0.62 ft-lb/in	0.75 ft-lb/in

- The above data (other than Dow's data) is an average of at least 10 samples for each test with acceptable S.D. of 5% or better.



Shaw Industries i-PP/Me8T8 Fiber



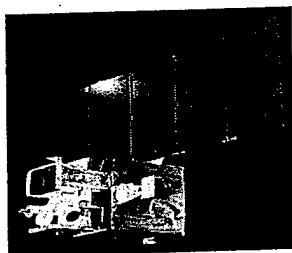
Nanodispersion of Me8T8 around defect/dirt?

POSS-iPP Summary

Prof. Ben Hsiao: SWAXS Studies

- 1) Some evidence of molecular dispersion of POSS in iPP - probably due to the favorable entropy of mixing between R (-CH₃) and the iPP chains
- 2) Half time of crystallization decreases by two orders of magnitude by flow (10² vs. 10⁴ s). The addition of POSS further reduced the crystallization time - an indication of POSS being true molecular orientation enhancing agents (real nanocomposites)
- 3) In typical polymer processing, only the chains longer than M* can be oriented; chains shorter than M* remain unoriented due to fast relaxation. The addition of POSS appears to reduce the value of M* - more studies are needed!

Goal: Develop Multi-Functional, Space-Survivable Materials



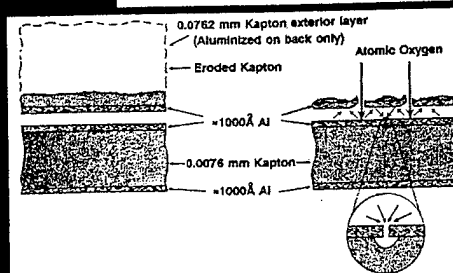
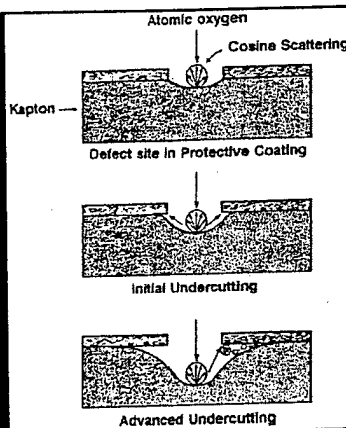
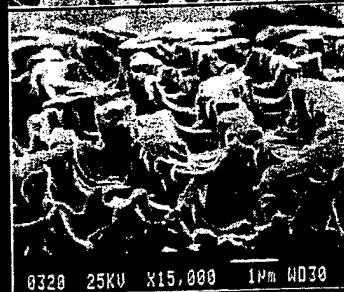
Satellites & Space Systems

Bond	Dissociation Energy (EV)	λ (nm)	Material
$-\text{C}_6\text{H}_4-\text{C}(=\text{O})-$	3.9	320	Kapton®
C-N	3.2	390	Kapton®
CF_3-CF_3	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

Objectives

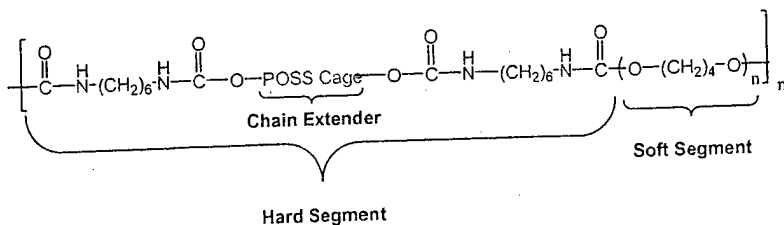
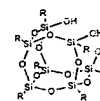
- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials by 10x
- Self-Passivating/Self-Rigidizing/Self-Healing based on nanocomposite incorporation

AO undercutting of LDEF Aluminized-Kapton Multilayer Insulation



Groh, K.K., Banks, B.A., J. Spacecraft and Rockets, Vol. 31, No. 4, 656-664 (1994)

POSS-polyurethane Properties



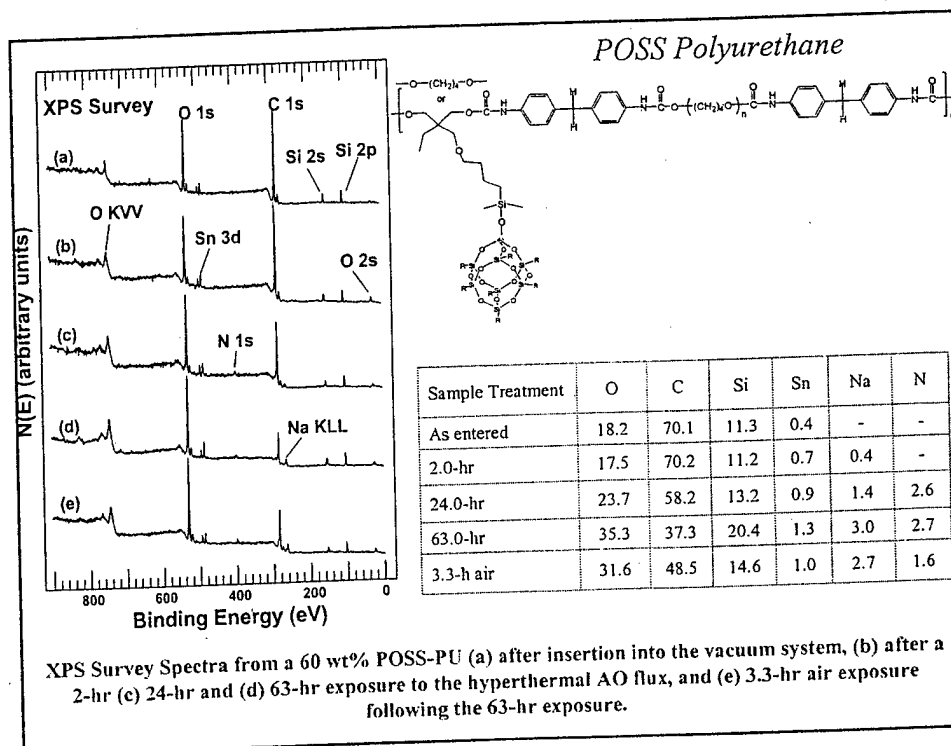
POSS-polymer improvements

Up to 300 °C increase in the melt transition temperature (rheological studies show the transition from an oil to a true thermoplastic elastomer)

Up to a 100 °C increase in T_{dec} (29 wt% POSS, still TPE)

Up to 10X increase in moduli (>400% elongation with no destruction of hard segments))

17% POSS incorporation ----> 3X increase in Hardness (Shore A)



Summary

- Successfully demonstrated multi-functionality of POSS utilizing both mechanical and physical properties
- We are looking into multiple applications for inorganic particles both as blends and copolymers
- Hybrid Plastics has been extremely successful in reducing the cost and increasing the production of POSS monomers
- Only with continued development of POSS monomers can we hope to control/predict property enhancements